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JC07 Rec'd PCT/PTO 25 JAN 2002

FORM PTO-1390 (REV 12-2001) U S DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE		ATTORNEY'S DOCKET NUMBER 514453-3912
TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371		U S APPLICATION NO (If known see 37 C F R 1 5) 10/048104
INTERNATIONAL APPLICATION NO. **PCT/EP00/07075**	INTERNATIONAL FILING DATE **24 JULY 2000**	PRIORITY DATE CLAIMED **28 JULY 1999**

TITLE OF INVENTION **SMECTIC LIQUID CRYSTAL HIGH-CONTRAST CONTROL OR DISPLAY DEVICE**

APPLICANT(S) FOR DO/EO/US **Hans-Rolf DÜBAL, Barbara HORNUNG, Toshiaki NONAKA**

Applicants herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information·

1 ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C 371

2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U S.C 371.

3. ☐ This is an express request to promptly begin national examination procedures (35 U.S C. 371(f)). The submission must include items (5), (6), (9) and (21) indicated below

4 ☒ The US has been elected by the expiration of 19 months from the priority date (PCT Article 31)

5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2))

- a. ☒ is attached hereto (required only if not communicated by the International Bureau).
- b ☐ has been communicated by the International Bureau.
- c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US)

6 ☒ An English language translation of the International Application as filed (35 U.S.C 371(c)(2)).

- a. ☒ is attached hereto.
- b. ☐ has been previously submitted under 35 U.S.C. 154(d)(4).

7. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))

- a ☐ are attached hereto (required only if not communicated by the International Bureau).
- b. ☐ have been communicated by the International Bureau.
- c ☐ have not been made; however, the time limit for making such amendments has NOT expired.
- d. ☒ have not been made and will not be made.

8. ☐ A English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3))

9 ☐ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).

10 ☐ An English language translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U S.C. 371(c)(5)).

Items 11 to 20 below concern document(s) or information included:

11. ☒ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.

12. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.

13. ☐ A FIRST preliminary amendment.

14. ☐ A SECOND or SUBSEQUENT preliminary amendment.

15. ☐ A substitute specification.

16. ☐ A change of power of attorney and/or address letter.

17 ☐ A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C 1.821 – 1.825.

18. ☐ A second copy of the published international application under 35 U S.C. 154(d)(4).

19 ☐ A second copy of the English language translation of the international application under 35 U.S.C 154(d)(4)

20. ☒ Other items or information·

PCT/IB/304, PCT/IPEA/402, 409, 416
PCT/ISA/210, 3 sheets of drawings, 1 page Abstract

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Date of Deposit **January 25, 2002**

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531 Rec'd PCT/PTO 25 JAN 2002

U S APPLICATION NO (If known, see 37 CFR 1 5) 10/048104	INTERNATIONAL APPLICATION NO PCT/EP00/07075	ATTORNEY'S DOCKET NO 514453-3912

21 ☒ The following fees are submitted				CALCULATIONS	PTO USE ONLY
BASIC NATIONAL FEE (37 CFR 1.492(a)(1)-(5): Neither international preliminary examination fee (37 CFR 1 482) nor international search fee (37CFR 1 445(a)(2) paid to USPTO and International Search Report not prepared by the EPO or JPO . . . . $1040 00 International preliminary examination fee (37 C F.R 1 482) not paid to USPTO but International Search Report prepared by the EPO or JPO . . . . . . $890.00 International preliminary examination fee (37 CFR 1 482) not paid to USPTO but international search fee (37 CFR 1 445(a)(2)) paid to USPTO . . . . . . $740.00 International preliminary examination fee paid to USPTO (37 CFR 1.482) but all claims did not satisfy provisions of PCT Article 33(1)-(4 . . . . . . $710 00 International preliminary examination fee paid to USPTO (37 CFR 1 482) and all claims satisfied provisions of PCT Article 33(1)-(4) $100 00					
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Surcharge of **$130.00** for furnishing the oath or declaration later than ☐ 20 ☐ 30 months from the earliest claimed priority date (37 CFR 1.492(e)).				$	
CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE	$	
Total Claims	11 - 20 =	0	x **$18.00**	**$ 0.00**	
Independent Claims	5 - 3 =	2	x **$84.00**	**$ 168.00**	
MULTIPLE DEPENDENT CLAIM(S) (if applicable)			+ **$280.00**	$	
TOTAL OF ABOVE CALCULATIONS =				$	
☐ Applicant claims small entity status See 37 C F R. 1.27. The fees indicated above are reduced by ½. +				$	
SUBTOTAL =				$	
Processing fee of **$130.00** for furnishing the English translation later than ☐ 20 ☐ 30 months from the earliest claimed priority date (37 CFR 1.492(f))				$	
TOTAL NATIONAL FEE =				$	
Fee for recording the enclosed assignments (37 CFR 1 21(h)) The assignment must be accompanied by an appropriate cover sheet (37 CFR 3 28, 3 31) **$40.00** per property +				$	
TOTAL FEES ENCLOSED =				**$1058.00**	
				Amount to be refunded:	$
				charged:	$

a. ☒ A check in the amount of $1058.00 to cover the above fees is enclosed.

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NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO:

Reg. No. 37,514
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28,029
REGISTRATION NUMBER

Dated: January 25, 2002

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514453-3912
PATENT

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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicants	:	Dübal et al.
U.S. Serial No.	:	10/048,104
International Application No.	:	PCT/EP00/07075
Title of Invention	:	SMECTIC LIQUID CRYSTAL HIGH-CONTRAST OR DISPLAY DEVICE
International Filing Date	:	July 24, 2000
Examiner	:	N/A
Group Art Unit	:	N/A

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Date of Deposit April 22, 2002

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PRELIMINARY AMENDMENT

Assistant Commissioner for Patents
Washington, D.C. 20231

Sir:

Prior to examining the above-identified application on the merits, kindly amend the application as follows:

00062949.DOC

IN THE CLAIMS:

Kindly cancel all the claims, without prejudice or the intention of creating estoppel, and substitute:

--12. A liquid-crystal switching or display device comprising a chiral smectic liquid-crystal mixture in monostable alignment, characterized in that the ratio Δ/Θ of the angle between the rubbing direction and the smectic layer normal to the tilt angle in the liquid-crystal mixture is at least 0.41, or in that the liquid-crystal mixture has the phase sequence I-N-C and the angle ρ between the rubbing direction and the monostable position is at least 1°, or in that the liquid-crystal mixture has the phase sequence I-N-C and the difference of the tilt angles measured at 15°C and 5°C below Tc, the upper limit of the range of existence of the optically active smectic phase, is less than 9.5°.

13. A liquid-crystal switching or display device as claimed in claim 12, characterized in that the liquid-crystal mixture has the phase sequence I-N-C and the tilt angle Θ at 25°C is between 19° and 39°.

14. A liquid-crystal switching or display device as claimed in claim 12, characterized in that the mixture has a spontaneous polarization of less than 150 nC/cm^2.

15. A liquid-crystal switching or display device as claimed in claim 12, characterized in that the device is an active-matrix or passive-matrix display.

16. A liquid-crystal switching or display device as claimed in claim 12, wherein the chiral smectic liquid-crystal mixture has the following properties:

phase sequence I-N-C and

Tc greater than 50°C and

T_{NI} less than 105°C and

19° < tilt angle (25°C) < 39° and

spontaneous polarization less than 150 nC/cm^2 and

pitch of the cholesteric helix greater than 2 μm and

the difference of the tilt angles measured at 15°C and 5°C below Tc, the upper limit of the range of existence of the optically active smectic phase, is less than 9.5°.

17. The device as claimed in claim 16, characterized in that the chiral smectic liquid crystal mixture comprises of nitrogen- or sulfur-containing heterocyclic compounds in an amount which is at least 20% by weight of total said mixture.

18. The device as claimed in claim 17, characterized in that the chiral smectic liquid crystal mixture comprises at least one sulfur-containing heterocyclic compound which is a thiophene derivative.

19. A chiral smectic liquid-crystal mixture having the phase sequence I-N-C, characterized in that the addition of 10% by weight, based on the total mixture, of a smectic A inducer leads to the occurrence of an smA phase range of less than 5.5°C, and the addition of 25% by weight, based on the total mixture, leads to the occurrence of an smA phase range of at least 0.1°C.--

REMARKS

This invention relates generally to smectic liquid-crystal displays. Specifically, the invention of the current application provides a suitable chiral smectic liquid crystal mixture and a switching and display device comprising the suitable chiral smectic liquid-crystal mixture, where the liquid-crystal mixture makes it possible, owing to its excellent alignment properties and specified favorable alignment angles, to achieve a very high contrast over a broad temperature range.

This Amendment cancels all claims (1-11) in favor of new claims 12-19. Support for these new claims is found throughout the body of the application and no new subject is believed

to be added by the new claims. Further, as these claims do not narrow the scope of the claimed subject matter, the application of the doctrine of equivalents is not affected. It is believed that no fee is required for the consideration of the Amendment. If, however, a fee is due, the Assistant Commissioner is authorized to charge such fee, or credit any overpayment to Deposit Account No. 50-0320.

Favorable action is earnestly solicited.

Respectfully submitted,

FROMMER LAWRENCE & HAUG LLP
Attorneys for Applicants

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3/PRTS

10/048104
531 Rec'd PCT/PTO 25 JAN 2002

"as originally filed"

High-contrast smectic liquid-crystal switching or display device

Displays or electro-optical display devices based on smectic liquid-crystal mixtures as electro-optically active layer are gaining in importance owing to their high response speeds.

The use of smectic liquid crystals in electro-optical or fully optical components requires either compounds which form tilted or orthogonal smectic phases and are themselves optically active, or the induction of ferroelectric or electroclinically active smectic phases by doping, with optically active compounds, of compounds which, although forming such smectic phases, are not themselves optically active. The desired phase should also be stable over the broadest possible temperature range to ensure that the display has a broad operating range. In particular, the achievable contrast should be as high as possible over the entire operating range. Liquid-crystal displays may be operated in principle as active- or passive- matrix display.

In what is known as active-matrix technology (AMLCD), a nonstructured substrate is usually combined with an active-matrix substrate. An electrically non-linear element, for example a thin-film transistor, is integrated into each pixel of the active-matrix substrate. The non-linear elements can also be diodes, metal-insulator-metal and similar elements, which are advantageously produced by thin-film processes and are described in the relevant literature (see, for example, T. Tsukuda, TFT/LCD: Liquid Crystal Displays Addressed by Thin-Film Transistors, Gordon and Breach 1996, ISBN 2-919875-01-9, and the references cited therein).

Active-matrix LCDs are usually operated with nematic liquid crystals in TN (twisted nematics), ECB (electrically controlled birefringence), VA (vertically aligned), IPS (in-plane switching) or OCB (optically compensated bend) mode. In each case, the active matrix generates an electric field of individual strength on each pixel, producing a change in alignment and thus a change in birefringence, which is in turn optically visible in polarized light. A severe disadvantage of these processes is the poor video capability, i.e. the excessively slow response times of nematic liquid crystals. In particular, nematic LCDs are not capable of displaying sharp moving pictures, as described, for example, in Sueoka et al (K. Sueoka, H. Nakamura and Y. Taira, SID 1997, p. 203-206, ISSN 1083-1312/97/1701-0203).

For this and other reasons, liquid-crystal displays based on the combination of ferroelectric liquid-crystal materials and active-matrix elements have been proposed, for example in WO 97/12355 or in Ferroelectrics 1996, 179, 141-152, or by W.J.A.M. Hartmann (IEEE Trans. Electron. Devices 1989, 36, 9; Pt. 1, pp. 1895-9, and Dissertation, Eindhoven, The Netherlands, 1990), which, however, were never brought to practical maturity owing to a limited temperature range and difficult reproducibility of the smectic texture.

While Hartmann utilizes the charge-controlled bistability to display a virtually continuous gray scale, Nito et al. have suggested a monostable FLC geometry (Journal of the SID, 1/2, 1993, pp. 163-169) in which the FLC material is aligned by means of relatively high voltages such that only a single stable position results from which a number of intermediate states are then generated by application of an electric field via a thin-film transistor. These intermediate states correspond to a number of different brightness values (gray shades) when the cell geometry is matched between crossed polarizers.

The disadvantage of the paper by Nito et al. is the occurrence of a streaky texture which limits the contrast and brightness of this cell (see fig. 8 of the abovementioned citation). Furthermore, this method produces switching only in an angle range of up to a maximum of once the tilt angle, which is about 22° in the case of the material used by Nito et al. (cf. p. 165, fig. 6) and thus produces a maximum transmission of only 50% of the transmission of two parallel polarizers.

Terada et al. have suggested a monostable FLC configuration (Terada, M., Togano, T., Asao, Y., Moriyama, T., Nakamura, S., Iba, J., presented at the Applied Physics Conference, March 28, 1999, Tokyo, Japan; Abstract No. 28p-V-8). With respect to the phases, Terada et al define the sequence I-N-C as "sufficient". However, these prototypes are not yet suitable for practical use over a relatively large temperature range. One reason for this is that, in practice, I-N-C is a necessary, but not a sufficient condition, and suitability for practical use places a number of additional conditions on the liquid crystal.

It is an object of the present invention to provide a suitable chiral smectic liquid-crystal mixture and a switching and display device comprising such a suitable chiral smectic liquid-crystal mixture, where the liquid-crystal mixture makes it possible, owing to its excellent alignment properties and specified favorable alignment angles, to achieve a very high contrast over a broad temperature range.

A precondition for a very high contrast over a broad temperature range is an extremely small dark transmission of the LCD cell. This is in turn achieved, on the one hand, only when the mixture has excellent alignment properties, because any defect or local deviation of the director from the dark position reduces the contrast significantly, and, on the other hand, when the alignment varies only slightly with temperature. This applies in particular when considering a broad operating temperature range, e.g. from –10°C to +60°C, preferably from 0°C to +55°C, in particular from 10°C to 50°C.

This object is achieved according to the invention by a liquid-crystal switching or display device comprising a chiral smectic liquid-crystal mixture, characterized in that the ratio Δ/Θ of the angle between the rubbing direction and the smectic layer normal to the tilt angle in the liquid-crystal mixture is at least 0.41.

Preferably, the object is achieved by a chiral smectic switching or display device which utilizes a chiral smectic liquid-crystal mixture having the phase sequence I-N-C, the symbols having the following meaning:
I = isotropic phase
N = nematic or cholesteric phase
C = smectic C phase (including all sub-types of the C phase) or another tilted phase, chiral or containing chiral dopants (the symbol * which is customary in the literature is omitted for the sake of simplicity of representation), and the alignment being such that the angle ratio w, defined as

$$w = \Delta/\Theta \text{ is at least 0.41, where}$$

Δ is the angle between the rubbing direction (Fig. 1, axis 1) and the smectic layer normal (Fig. 1, axis 2), where the term rubbing direction includes a preferential direction obtained by other processes than a rubbing treatment, e.g. photo-alignment or the like, and Θ is the tilt angle, preferably determined by the response behavior by means of electric voltages or X-ray analysis (Fig. 1, axes 2 and 4‘ or 2 and 4, respectively).

Preference is given to w values of at least 0.45, particularly preferably > 0.53, in particular between 0.55 and 0.99, most particularly between 0.60 and 0.85.

Particularly preferaby, w is at least 0.41 while simultaneously limiting the tilt angle range to 19° to 39°, preferably 20° to 36°, particularly preferably 22° to 34°, most preferably 23° to 33°, in particular 24° to 32° (at 25 °C).

Moreover, the object is achieved according to the invention by a chiral smectic liquid-crystal switching or display device comprising a chiral smectic liquid-crystal mixture having the phase sequence I-N-C in monostable alignment, the alignment being such that the angle ρ between the rubbing direction and the monostable position (maximum dark position, axes 1 and 3 in Fig. 1) is at least 1°, preferably at least 1.3°, particularly preferably at least 1.6°, in particular at least 1.9°.

Preference is given to combinations of the features of the first and second, first and third, second and third, or first, second and third above-described embodiments of the liquid-crystal switching and display device of the invention.

Particularly preferaby, w is at least 0.41 while simultaneously having an angle ρ of more than 1°.

Particularly preferaby, w is at least 0.41 while simultaneously limiting the tilt angle range to 19° to 39° (at 25°C) and, as additional condition, having an angle ρ of more than 1°.

Particularly preferably, w is at least 0.41 while simultaneously limiting the tilt angle range to 19° to 39° (at 25°C), having an angle ρ of more than 1° and, as additional condition, having a spontaneous polarization of < 150 nC/cm².

Preference is given to a mixture having the phase sequence I-N-C whose spontaneous polarization in the operating temperature range is <150 nC/cm², particularly preferably <70 nC/cm², very particularly preferably <35 nC/cm², in particular <15 nC/cm², most particularly in the range from 4.1 to 9.9 nC/cm².

Such displays exhibit a virtually or completely defect-free alignment and a dark position which is very dark, and thus have a high contrast over a broad temperature

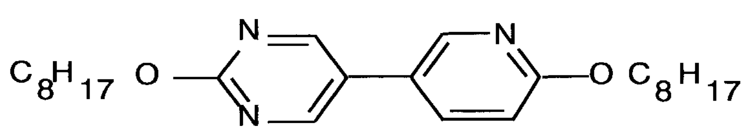
range. Examples of such displays are active-matrix displays or passive-matrix displays.

The object is likewise achieved according to the invention by a chiral smectic switching or display device, in particular by an active-matrix display containing a liquid-crystal mixture and by the liquid-crystal mixture itself which have the phase (transition) sequence

$$I - N - C$$

having a moderately, i.e. not too weakly and not too strongly, suppressed smectic A phase which manifests itself by one or both of the following features:

- increasing the concentration of at least one component of the mixture which induces a smectic A phase by 25% by weight, based on the total mixture, leads to the occurrence of a significant smA phase range in the mixture, whereas increasing the concentration by only 5% by weight does not lead to the occurrence of an smA phase, or
- the addition of ten (10) % by weight, based on the total mixture, of a smectic A inducer, preferably component A, CAS registration no. 156682-16-5, designation: 5-[6-(octyloxy)-3-pyridinyl]-2-(octyloxy) pyrimidine



leads to the occurrence of an smA phase range of less than 5.5°C (phase width), but of at least 0.1°C on addition of 25% by weight, bases on the total mixture, of component A.

The invention furthermore relates to a process for finding suitable liquid-crystal mixtures which comprises the abovementioned process steps.

Furthermore, the LCD cell is advantageously asymmetrical, i.e. the top surface and the bottom surface of the cell differ in at least one feature apart from a possible active-matrix construction (thin-film transistor) itself. This is in particular the case:

- when using unsymmetrical or unsymmetrically treated alignment layers (for example in the case of antiparallel rubbing)
- when one of the two alignment layers is omitted
- when the step of rubbing one of the two alignment layers is omitted or changed
- when an unsymmetrical layer structure is introduced, for example by additional insulation layers having different properties on their top and bottom surfaces
- with all measures which finally result in exposure of the liquid-crystal domain to an unsymmetrical environment in relation to a symmetry plane parallel to the electrode surfaces.

Expressly included is the advantageous use of the novel materials and mixtures for active-matrix displays, antiferroelectric displays and smectic displays, the term "display" being intended to mean any type of optical display or switching device regardless of its size, structure, light guidance, addressing and use.

In particular, the term "active-matrix display" as used herein includes an LCD in which one of the two substrates is replaced by the rear side of an IC chip (IC = integrated circuit) as described, for example, in D.M. Walba, Science 270, 250-251 (1995) or http://www.displaytech.com, i.e. the LCOS (LC On Silicon) technology.

In particular, the term “active-matrix display” as used herein includes an LCD in which one of the two substrates is replaced by the rear side of a plasma cell (plasma-addressed LCD).

In general, preference is given to displays having an electrode separation of 0.7 to 3.0 µm, in particular active-matrix displays having an electrode separation of 0.8 to 2.0 µm, which contain a chiral smectic mixture exhibiting a weakly suppressed smA phase.

Particular preference is given to a display utilizing pulsed or rapidly changing backlight (“sequential backlight” technology).

The object is likewise achieved by the use of a chiral smectic liquid-crystal mixture having the phase sequence I-N-C as electro-optically active layer in monostable switching and display devices or displays, characterized in that the chiral smectic liquid-crystal mixture has the following combination of properties:

TC greater than 50 °C and

T_{NI} less than 105 °C and

19° < tilt angle (25°C) < 39 ° and

spontaneous polarization less than 150 nC/cm² and

pitch of the cholesteric helix greater than 2 µm and

the difference of the tilt angles measured at 15°C and 5°C below Tc, the upper limit of the range of existence of the optically active smectic phase, is less than 9.5°. It is advantageous that the (total) content of N- and/or S-heterocyclic compounds in the mixture is at least 20% by weight. Particular preference is given to thiophene derivatives.

In the drawing:

Fig. 1 is a schematic representation of the position of the respective angles used relative to one another

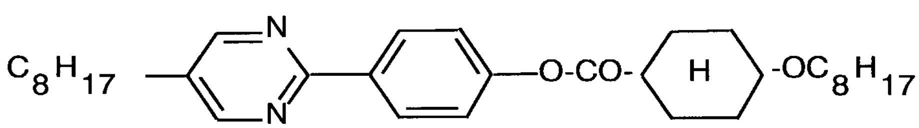
Fig. 2 is the phase diagram for Example 1

Fig. 3 is the optical transmission of a test cell as a function of the voltage for a mixture from Example 6.

The invention is explained in greater detail by the examples below.

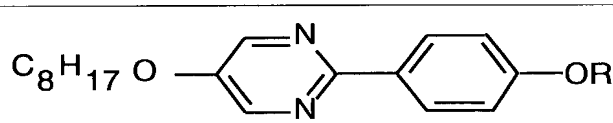
Example 1

To illustrate the moderately suppressed smA phase, a mixture is prepared from a mixture M1 and component B:



The concentration of component B is continuously varied. In this way, a two-dimensional portion of the phase diagram of the mixture is obtained which is depicted in Fig. 2.

Table 1: Composition of test mixture M1:

	% by weight
R = C_8H_{17}	14.43
R = C_6H_{13}	29.12
R = C_4H_9	28.47
R = $C_{10}H_{21}$	27.98
total % by weight	100.00

The NAC tricritical point occurs at ([M1]=66% by weight, [B]=34% by weight) as depicted in Fig.2 (in Fig.2, T denotes the temperature in degrees Celsius, [B] the weight percentage of component B, based on the total mixture). I, N, C have been defined above. A denotes smectic-A phase. The vicinity of the NAC point according to the invention is determined as follows.

Six test mixtures having the following compositions are prepared:

Table 2: Test mixtures P-U and phase sequences thereof

Mixture	[M1]	[B]	Phase sequence
	% by weight		Phases, temperature in °C
P	75	25	C 85.3 A 90,6 N 108 I
Q	66	34	C 85.6 (NAC) 85.6 N 115 I
R	60	40	C 85.6 N 116 I
S	55	45	C 86,5 N 119 I
T	50	50	C 87 N 122 I
U	20	80	C 92.7 N 145 I

The resulting mixtures are admixed with 10% by weight of component A (as defined above) as smA inducer. The following phase ranges are obtained:

Table 3: Test mixtures PA-UA and phase sequences thereof following addition of component A (see above, 10% by weight)

Mixture	90 wt%	Phase sequence with 10 wt% of A	Width of smA-phase
		Phases, temperature in °C	°C
PA	P	C 82.6 A 94.3 N 103 I	11.7
QA	Q	C 85.5 A 93.0 N 106 I	7.5
RA	R	C 86.8 A 92.5 N 109 I	5.7
SA	S	C 88.2 A 90.6 N 112 I	2.4
TA	T	C 88.5 (NAC) 88.5 N 114 I	0.0
UA	U	No smA phase	0.0

These data show that the mixtures U,T,S are within the preferred range of the present invention as they are far enough away from the NAC multicritical point and the smA phase is sufficiently strongly suppressed. In particular, smA phase ranges of more than 0.1°C occur in the mixtures T, S and U upon addition of 25% of component A.

The spontaneous polarization can be adjusted to virtually any value by addition of a suitable chiral substance or substance mixture. For example, the addition of 5% by weight of component C8 (see Example 3 below) to mixture T gives a chiral smectic mixture having the phase sequence

I 115 N 84 C.

having Ps= -7,8 nC/cm² and a tilt angle of 27° at 25°C.

Example 2 LCD test cell

An LCD test cell is prepared from two commercially available glass plates which are transparently and conductively coated with indium-tin oxide. The plates are spin-coated (2500 rpm, 10 s) with the alignment layer LQT-120 (from Hitachi Chemicals KK) which was diluted to 8.3% of its original solids content using N-methylpyrrolidone, cured by heating (230°C, 1 h) and then aligned by subjecting them to a rubbing process (rubbing material: rayon type YA-20-R*, clearance 0.2 mm, once, roller speed 700 rpm, substrate speed 10 cm/s, roller diameter 10 cm).

The rubbed glass plates are arranged such that the rubbing direction is antiparallel, adhesively bonded to produce test cells and set 1.3 μm apart by means of a spacer.

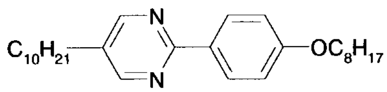
The FLC mixture is introduced into the cell and initially aligned in the nematic or cholesteric phase by cooling. On further cooling, a 3 Volt direct voltage is applied and the cell is transferred into the smC phase (chiral smectic C) range at a cooling rate of 2 K/min. During this process, a monstable domain is formed when mixtures according to the invention are used.

The rubbing direction, if it is not known anyway, can be determined experimentally by transfer into the nematic phase by heating and subsequent determination of the dark position between crossed polarizers.

The tilt angle can be determined experimentally by switching the cell at operating temperature. Here, a saturation of the optical transmissions at positive and negative voltage (typically 20 V) is observed which are associated with specific angles of rotation (Fig. 1, axes 4, 4‘). The angle difference at saturation gives the value 2Θ (=twice the tilt angle), the angle bisector gives the layer normal (Fig. 1, axis 2). The dark position can be determined easily.

Example 3

Test mixtures are prepared from the following components C1-C8 (mixtures V,W,X, see Table 4). The phase transitions and some properties of the cell described in Example 2 and produced using these mixtures are summarized in Table 5.



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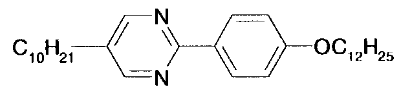

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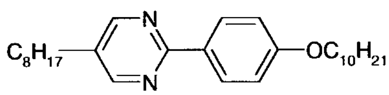

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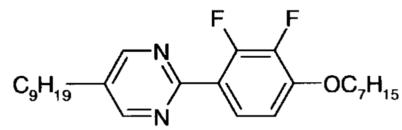

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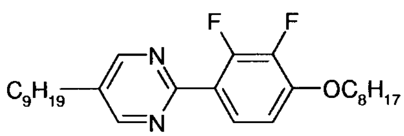

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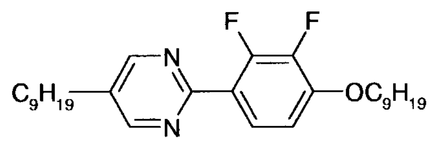

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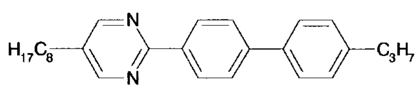
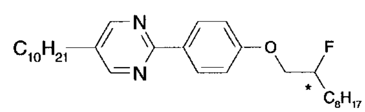


component C7



component C8

Table 4: Compositions of mixtures V,W,X

Component	V	W	X
C1	14.4%	7.2%	
C2	14.4%	7.2%	
C3	14.4%	7.2%	
C4	14.4%	21.6%	28.8%
C5	14.4%	21.6%	28.8%
C6	14.4%	21.6%	28.8%
C7	10.0%	10.0%	10.0%
C8	3.6%	3.6%	3.6%

Table 5: Properties of the chiral smectic mixtures and of the cell produced by the method described in Example 2

				10V, 60Hz					
Mixture	Tc	ΔSa	Ps (nC/cm²) 25°C	Θ_{Tc-10}	ρ	Σ	Σ/Θ	Δ	w= Δ/Θ
V	62.8	1.5	3.7	19.9	-	19.9	1.0	0	0
W	56.1	0	4.8	23.1	3.6	13.7	0.59	9.4	0.41
X	59.2	0	5.9	23.9	4	12.2	0.51	11.7	0.49

The mixtures W and X have the phase sequence I-N-C and a Δ/Θ ratio of 0.41 (V) and 0.49 (W). In contrast, the use of mixture V having the phase sequence I-N-A-C does not result in advantageous utility for the purposes of the present invention.

Example 4

The mixtures W, X are admixed with component A, again such that the concentration of component A in these new mixtures is 10 percent by weight. The following smA phase widths (ΔSa) are obtained:

Table 6: smA phase range with 10% by weight of component A in °C

Mixture	Tc	ΔSa
W	59	4
X	62	2.5

These date show that the mixtures W and X have a sufficiently strongly suppressed smA phase which appears on addition of 10% of the smA inducer, and a width of

less than 5.5°C. On addition of 25% by weight of component A, SmA phase ranges of more than 0,1°C are obtained.

Example 5

The response properties of the test cells filled with the mixtures W and X (Table 2) are examined. To this end, the optical transmission between crossed polarizers is examined as a function of the applied voltage (bipolar pulse sequences having a frequency of 60 Hz = width of 8.3 ms). The following results were obtained at a temperature of 30°C:

Table 7: Analog gray scale using mixtures W and X

Voltage (Volt)	Transmission (%) Mixture W	Transmission (%) Mixture X
0	0	0
0.5	2	14.8
1	5.4	24.2
1.5	12	40.2
2	21.4	48.4
2.5	38.2	53.8
3	48.4	57.6
3.5	54	60.4
4	59.6	63.2
4.5	63.2	65
5	65.8	66.6
8	71.2	69.6
10	72.2	70

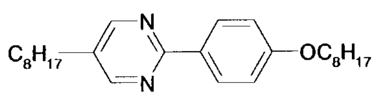
Response times (10 V) of mixture W: 0.22 ms (0-50%) or 0.15 ms (100-50%)

Response times (10 V) of mixture X: 0.20 ms (0-50%) or 0.12 ms (100-50%)

Both mixtures having a moderately, but sufficiently strongly suppressed smA phase can be utilized advantageously because an analog gray scale and submillisecond response at low values of spontaneous polarization are realized.

Example 6

Another eight test mixtures are prepared which contain the following components:



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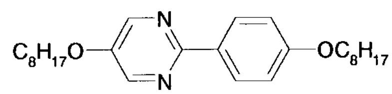

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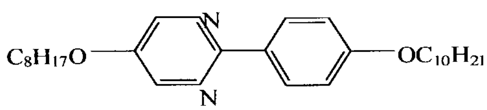

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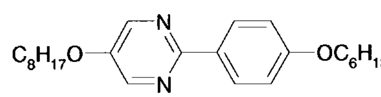

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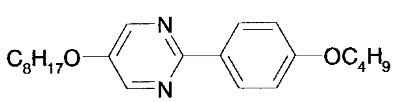

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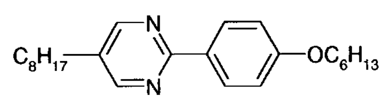
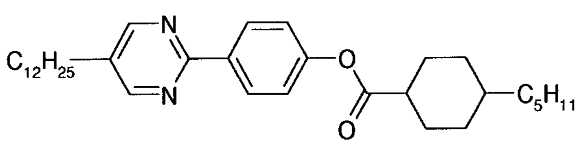


component C14



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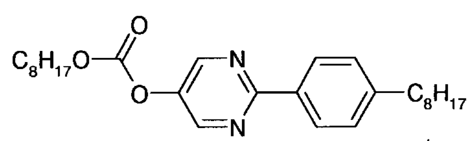
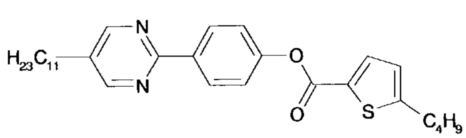


component C16



component C17

Table 8: Compositions of the test mixtures Y1 to Y8. Amounts are given in percent by weight.

Component	Y1	Y2	Y3	Y4	Y5	Y6	Y7	Y8
C9	8.5%	9.7%	10.8%	12.0%	13.0%	9.6%	8.5%	7.4%
C10	2.8%	3.2%	3.6%	4.0%	4.4%	3.2%	2.8%	2.5%
C3	6.8%	7.7%	8.6%	9.5%	10.4%	7.7%	6.8%	5.9%
C12	5.7%	6.5%	7.3%	8.1%	8.8%	6.5%	5.7%	5.0%
C13	5.6%	6.4%	7.1%	7.9%	8.6%	6.4%	5.6%	4.9%
C11	5.5%	6.3%	7.0%	7.8%	8.5%	6.3%	5.5%	4.8%
C14	8.8%	10.0%	11.1%	12.4%	13.5%	10.0%	8.8%	7.7%
C15	12.3%	14.0%	15.6%	17.3%	18.9%	13.9%	12.3%	10.7%
C16	10.0%	10.0%	10.0%	10.0%	10.0%	9.0%	7.9%	6.9%
C4	10.0%	7.5%	5.0%	2.5%	0.0%	4.5%	4.0%	3.4%
C6	10.0%	7.5%	5.0%	2.5%	0.0%	4.5%	4.0%	3.4%
C5	10.0%	7.5%	5.0%	2.5%	0.0%	4.5%	4.0%	3.4%
C17	0.0%	0.0%	0.0%	0.0%	0.0%	10.0%	20.0%	30.0%
C8	4.0%	4.0%	4.0%	4.0%	4.0%	4.0%	4.0%	4.0%

The mixtures Y1 to Y8 were now examined for their response properties, quality of alignment, temperature dependence of contrast and tilt angle, the angles as represented in Fig. 1, the angle ratio w and the extent of smectic A phase suppression. The experimental results are summarized in Table 9. In the table, the quantities TC (temperature dependence of contrast) and alignment were categorized by visual inspection and optical measurements into three classes (+ good, 0 medium, - bad). The quantity TT is determined from measurements of the temperature dependence of the tilt angle at 5°C ($\Theta 5$) and 15°C ($\Theta 15$) below T_C, the limit of the range of existence of smC. Then:

$$TT = (\Theta 15 - \Theta 5)/10.$$

The quantities Vo and Vs are defined in Fig. 3 (threshold voltage and saturation voltage, respectively). Fig. 3 depicts the optical transmission of a test cell as a function of the voltage for the mixture Y7 which is very suitable.

Table 9: Measured data for the test mixtures Y1 to Y8

Measured quantity [Unit]	**Y1**	**Y2**	**Y3**	**Y4**	**Y5**	**Y6**	**Y7**	**Y8**
T_{NI} [°C]	76	79	83	85	86	82	84	84
T_{NA} [°C]					68.8			
T_C [°C]	62.8	64.6	66.1	67.0	67.5	63.6	60.7	59.1
Δ smA [°C]	0	0	0	0	1.3	0	0	0
Θ [°] 20 V, Tc-30°C	29.5	28.3	27.6	26.0	23.7	28.2	29.0	29.6
Δ [°]	20.4	18.5	14.7	10.6	0	18.7	22.4	23.6
ρ [°]	3.4	3.5	3.3	3.5		3.0	2.2	3.0
Σ [°]	9.1	9.8	12.9	15.4	23.7	9.5	6.6	6
w = Δ / Θ	0.692	0.654	0.533	0.408	0.000	0.663	0.772	0.797
Σ / Θ	0.308	0.346	0.467	0.592	1.000	0.337	0.228	0.203
ρ / Σ	0.374	0.357	0.256	0.227		0.316	0.333	0.500
Δ smA* [°C] +10% comp. A	3.2	3.3	5.4	5.7	7.9	0.8	0.0	0.0
Vo [Volts]	0.8	0.7	0.3	1.0	-	0.8	1.0	0.3
Vs [Volts]	6	6	7	6	-	8	4.5	3.8
Alignment	+	+	0	0	-	+	+	+
TC (cf. text)	0	0	-	-	-	+	+	+
TT (cf. text)	0.61	0.62	0.72	0.95	0.75	0.49	0.38	0.29
Overall evaluation of the cell	+	+	0	-	-	+	+	+

Patent Claims

1. A liquid-crystal switching or display device comprising a chiral smectic liquid-crystal mixture, characterized in that the ratio Δ/Θ of the angle between the rubbing direction and the smectic layer normal to the tilt angle in the liquid-crystal mixture is at least 0.41.

2. A liquid-crystal switching or display device as claimed in claim 1, characterized in that the liquid-crystal mixture has the phase sequence I–N–C and the tilt angle Θ at 25°C is between 19° and 39°.

3. A liquid-crystal switching or display device comprising a chiral smectic liquid-crystal mixture having the phase sequence I-N-C in monostable alignment, characterized in that the angle ρ between the rubbing direction and the monostable position is at least 1°.

4. A liquid-crystal switching or display device comprising a chiral smectic liquid-crystal mixture having the phase sequence I-N-C in monostable alignment, characterized in that the difference of the tilt angles measured at 15°C and 5°C below Tc, the upper limit of the range of existence of the optically active smectic phase, is less than 9.5°.

5. A liquid-crystal switching or display device as claimed in one of claims 1 to 4, characterized in that the mixture has a spontaneous polarization of less than 150 nC/cm^2.

6. A liquid-crystal switching or display device as claimed in one of claims 1 to 4, characterized in that the device is an active-matrix or passive-matrix display.

7. The use of a chiral smectic liquid-crystal mixture having the phase sequence I-N-C as electro-optically active layer in monostable switching and display devices or displays, characterized in that the chiral smectic liquid-crystal mixture has the following properties:

T_C greater than 50°C and

T_{NI} less than 105°C and

19° < tilt angle (25°C) < 39° and

spontaneous polarization less than 150 nC/cm² and

pitch of the cholesteric helix greater than 2 µm and

the difference of the tilt angles measured at 15°C and 5°C below Tc, the upper limit of the range of existence of the optically active smectic phase, is less than 9.5°.

8. The use as claimed in claim 7, characterized in that the switching and display device is as defined in one of claims 1 to 6.

9. The use as claimed in claim 8, characterized in that the total content of nitrogen- or sulfur-containing heterocyclic compounds in the mixture is at least 20% by weight.

10. The use as claimed in claim 9, characterized in that the mixture contains at least one thiophene derivative.

11. A chiral smectic liquid-crystal mixture having the phase sequence I-N-C, characterized in that the addition of 10% by weight, based on the total mixture, of a smectic A inducer leads to the occurrence of an smA phase range of less than 5.5°C, and the addition of 25% by weight, based on the total mixture, leads to the occurrence of an smA phase range of at least 0.1°C.

Abstract

The liquid-crystal switching or display device comprises a chiral smectic liquid-crystal mixture, where the ratio Δ/Θ of the angle between the rubbing direction and the smectic layer normal to the tilt angle in the liquid-crystal mixture is at least 0.41. Preferably, the liquid-crystal mixture has the phase sequence I–N–C and the tilt angle Θ at 25°C is between 19° and 39°.

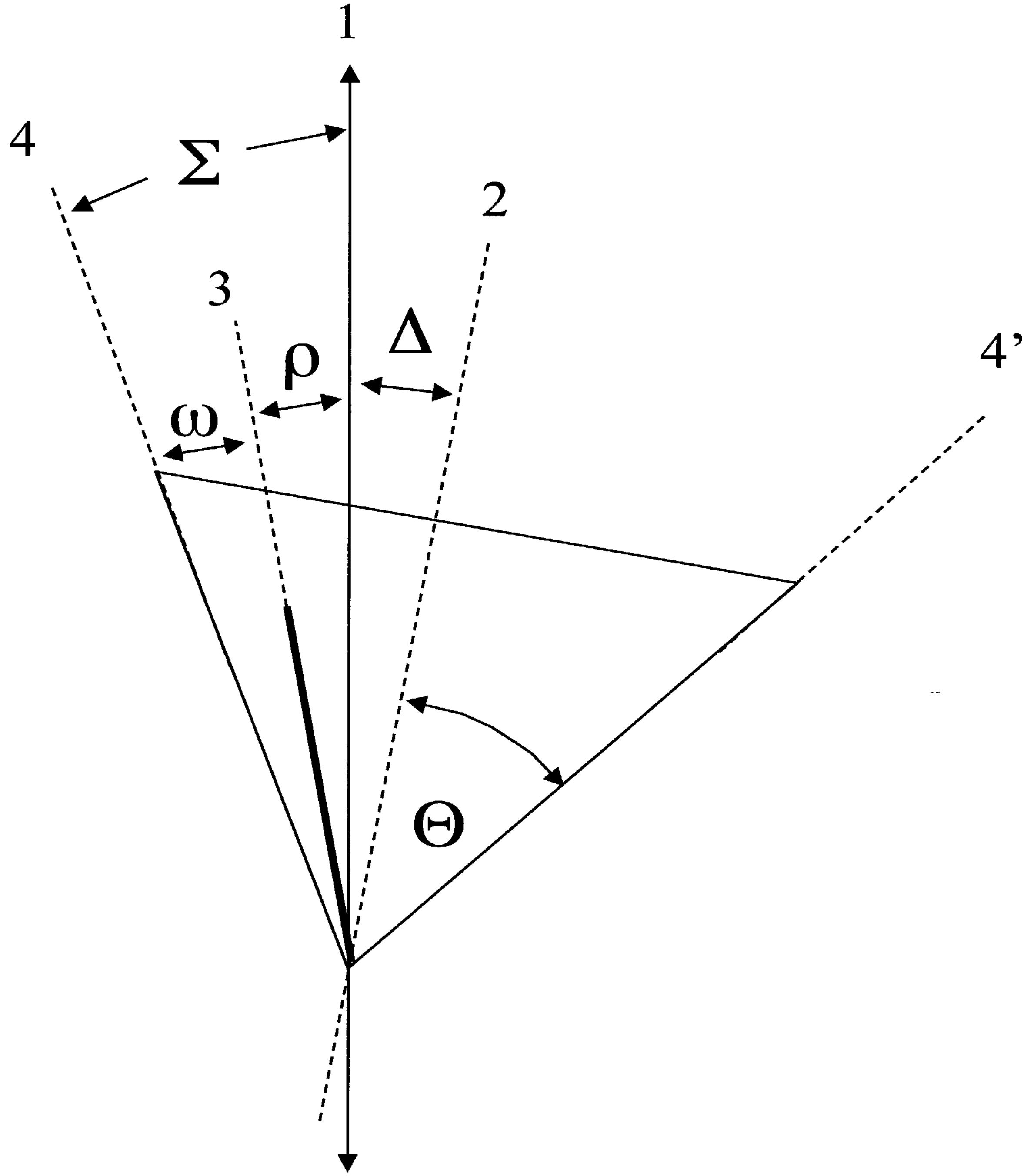


Fig. 1

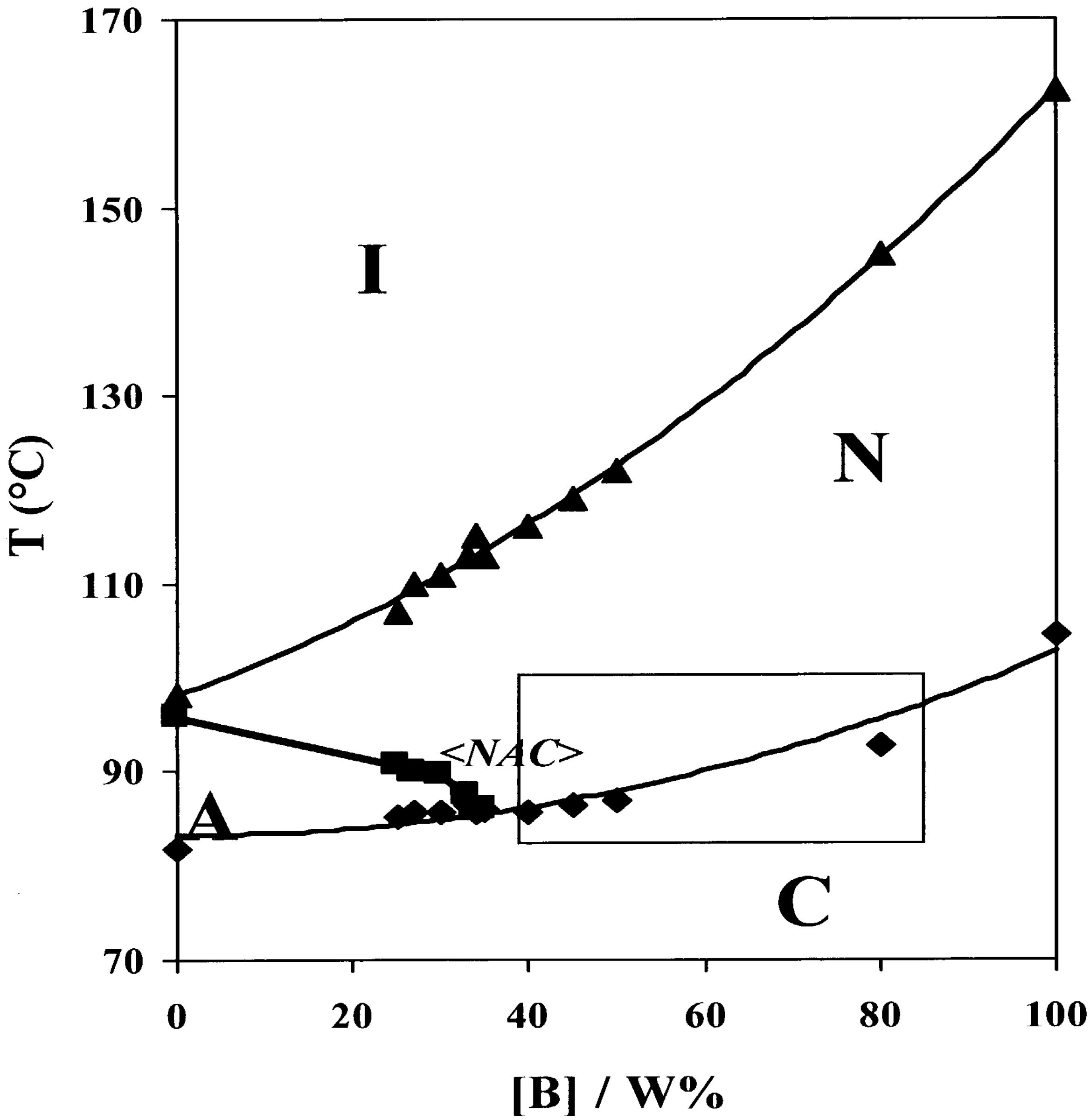


Fig. 2

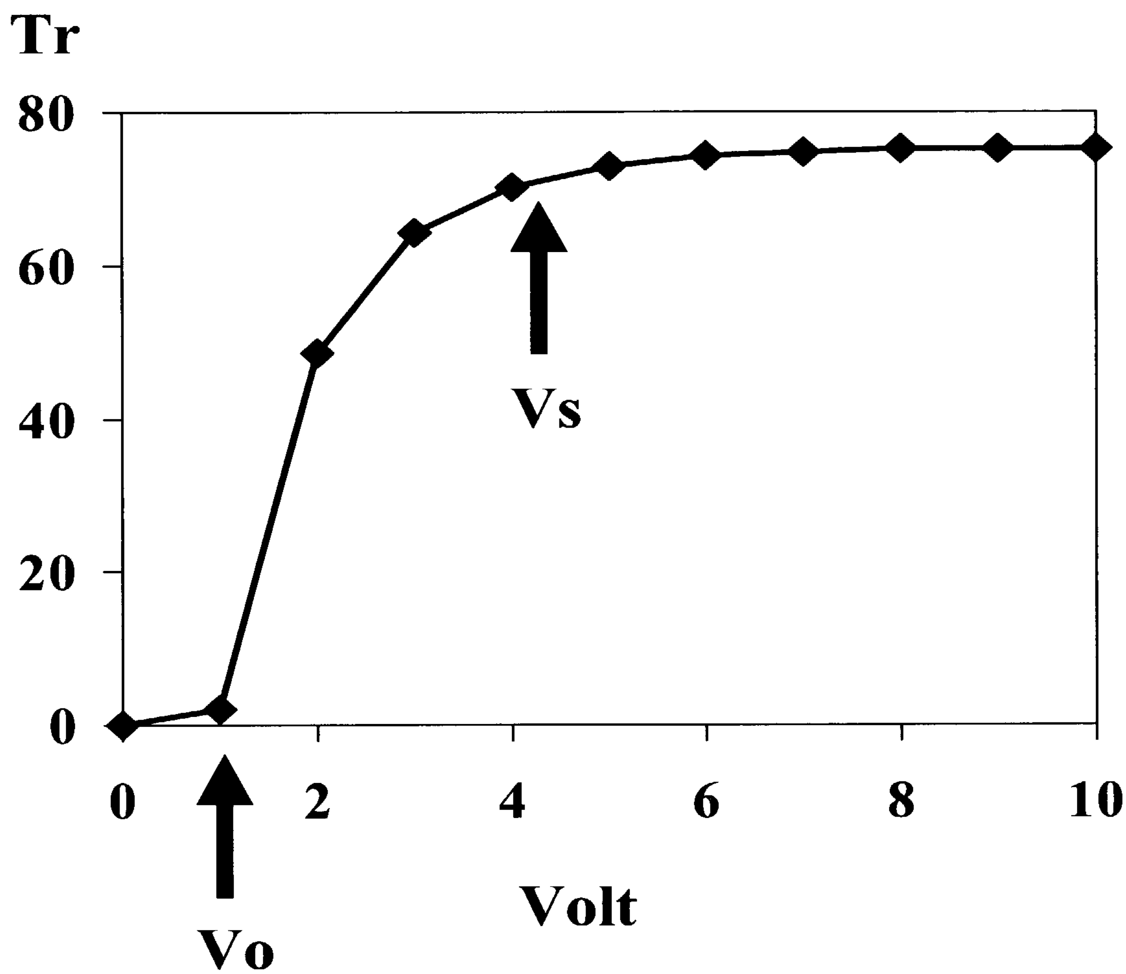


Fig. 3

Appln. Ser. No. 10/048,104
Filed: January 25, 2002

PATENT
514453-3912

DECLARATION FOR PATENT APPLICATION AND POWER OF ATTORNEY
(Includes reference to PCT International Applications)

FROMMER LAWRENCE & HAUG, LLP
File No.: 514453-3912

As a below named inventor, we hereby declare that:

Our residences, post office addresses and citizenships are as stated below next to our names.

We believe we are original, first and joint inventors (if plural, names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention ENTITLED:

SMECTIC LIQUID CRYSTAL HIGH-CONTRAST CONTROL OR DISPLAY DEVICE

the specification of which:

	is attached hereto
X	was filed on as:
X	United States Application Serial No.:
X	Corresponding to International Appln. No. PCT/EP00/07075 filed July 24, 2000 with amendments through DATE EVEN HEREWITH (if applicable, give details).

We hereby state that we have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

We acknowledge the duty to disclose to the United States Patent and Trademark Office all information known to our to be material to patentability as defined in Title 37, Code of Federal Regulations, § 1.56.

We hereby claim foreign priority benefits under Title 35, United States Code § 119 (a) - (d) or § 365 (b) of any foreign application(s) for patent or inventor's certificate, or § 365 (a) of any PCT International application(s) designating at least one country other than the United State of America listed below and have also identified below any foreign application for patent or inventor's certificate or any PCT International applications designating at least one country other than the United States of America filed by us on the same subject matter having a filing date before that of the application(s) on which priority is claimed:
Prior Foreign/PCT Application(s) [list additional applications on separate page]:

Country (or PCT)	Application Number:	Filed (Day/Month/Year)	Priority Claimed: Yes	No
Germany	199 34 798.0	28 July 1999	X	

We hereby claim the benefit under 35 U.S.C. § 119(e) of any United States provisional application(s) listed below.

We hereby claim the benefit under Title 35, United States Code § 120 of any United States application(s) or § 365 (c) of any PCT international application(s) designating the United States of America that is/are listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in that/those prior United States or PCT International application(s) in the manner provided by the first paragraph of Title 35, United States Code § 112, we acknowledge the duty to disclose to the United States Patent and Trademark Office all information known to us to be material to patentability as defined in Title 37, Code of Federal Regulations, § 1.56 which became available between the filing date of the prior application and the national or PCT international filing date of this application:

Prior U.S. (or U S.-designating PCT) Application(s) [list additional applications on separate page]:

U.S. Serial No..	Filed (Day/Month/Year)	PCT Application No.	Status (patented, pending, abandoned)

1

We hereby appoint William F. Lawrence, Registration No 28,029, ~~and~~ FROMMER LAWRENCE & HAUG, LLP or their duly appointed associates, our attorneys or agents, with full power of substitution and revocation, to prosecute this application, to

Appln. Ser. No. 10/048,104
Filed: Janaury 25, 2002

PATENT
514453-3912

make alterations and amendments therein, to file continuation and divisional applications thereof, to receive the Patent, and to transact all business in the Patent and Trademark Office and in the Courts in connection therewith, and to insert the Serial Number of the application in the space provided above, and specify that all communications about the application are to be directed to the following correspondence address.

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Direct all telephone calls to: (212) 588-0800
to the attention of:
William F. Lawrence

We hereby declare that all statements made herein of our own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

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